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Effect of biomass ash in catalytic fast pyrolysis of pine wood

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ABSTRACT

Fast pyrolysis experiments of pine wood have been performed in a continuously operated mechanically stirred bed reactor at 500 °C. The effects of the pine wood ash were studied by comparing non-catalytic and catalytic experiments (using a ZSM-5 based catalyst) with their ash-added counterparts. To show the case of ash accumulated from the biomass feeding, the results of catalytic fast pyrolysis obtained after eight reaction/catalyst regeneration cycles were included as well. The objective was to distinguish between the ash-catalyst interactions and the catalyst deactivation. The latter may be caused by thermo-mechanical, chemical and/or structural changes in the catalyst; such as poisoning, fouling, and attrition, as well as by coke deposition. Ash concentrations up to ca. 3 wt.% relative to the amount of pine wood fed, and ca. 0.002 wt.% relative to the amount of bed material, were found to be sufficient to change the distribution and the composition of pyrolysis products. The addition of ash to the catalytic fast pyrolysis, caused a reduction in the yields of both the organics and coke by 2 wt.% (on feed basis), while increases of 1 wt.% and 4 wt.% in the water and non-condensable gases were observed, respectively. The total yield of CO plus CO_2 was boosted by more than 10%, while the CO_2 production (decarboxylation reactions) was favoured clearly. Moreover, the presence of added-ash suppressed the conversion of sugars and acids – these were more pronounced in the case of accumulated-ash – as well as of the phenols. The catalyst deactivation during the reaction/regeneration cycles is not only related to the presence of ash but also to changes in the structure and composition of the catalyst. To overcome the drawbacks of biomass ash in catalytic fast pyrolysis, either the biomass feedstock has to be leached (ash removal) before being introduced to the process, or the char (which contains a vast majority of the biomass ash) has to be physically removed from the catalyst before the regeneration step.

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1. Introduction

Lignocellulosic biomass is an abundantly available, renewable resource of organic carbon and can be transformed into energy-dense alternative liquid fuels through fast pyrolysis. Fast pyrolysis is the thermal decomposition of the natural polymeric constituents of biomass in an oxygen-free atmosphere at temperatures around 500 °C. At optimal conditions, including high heating rates of the biomass particles, short vapour residence times and fast condensation of pyrolysis vapours, high yields of pyrolysis liquid (usually in the range of 60 to 70 wt.%, dry-feed basis) can be achieved.

However, some adverse properties of pyrolysis liquid limit its use in chemicals production and fuel applications. These include its high water content (15–30%), oxygen content (35–40 wt.%), corrosiveness (pH of 2–3), relatively low heating value compared to fossil fuels (ca. 17 MJ/kg), poor volatility and high viscosity. Hence, the quality of pyrolysis liquids must be improved before they can be considered as a liquid feed in the production of heat, electricity, transportation fuels and chemicals [1]. Catalytic fast pyrolysis (CFP), which is based on the use of heterogeneous catalysts in the fast pyrolysis process, intends to improve the quality of the liquid by steering the vapour phase reactions with respect to rates and selectivity.

In a CFP process, the inert heat transfer material is (partially) replaced by a solid catalyst. The presence of catalyst favours oxygen removal via decarbonylation (CO rejection), decarboxylation (CO_2 rejection) and dehydration (H_2O formation) reactions. The

ultimate composition of the produced liquids is influenced by factors such as the type of the biomass feedstock, the type of the catalyst (including pore size, acidity, nature of active sites and the presence of metals), optimal operating temperature of the catalyst, and the catalyst-to-feed ratio. In addition, the interaction between the volatiles generated by fast pyrolysis and the bed contents (e.g. catalyst, char, and ash) is an important feature of the pyrolysis reactor. More specifically, this interaction refers to reactions of reactive species present in the volatiles (including radicals generated by thermal cracking) with the char/ash particles [2]. Obviously, the selected catalyst should play a vital role in suppressing the production of undesirable oxygenated compounds (acids, sugars, poly-aromatic hydrocarbons, etc.) while promoting the production of value-added compounds (phenolics, alkanes, mono-aromatic hydrocarbons, etc.). Regarding the corresponding removal of oxygen, the preferred route from both, an energy-yield point of view and the desire to maintain a relatively high H/C ratio, must be decarboxylation [3,4].

One of the problems encountered in CFP is the deactivation of the catalyst which implies the physical, chemical, thermal, and mechanical degradation of the catalyst leading to a reduced activity and selectivity [5]. In CFP, deactivation mainly occurs by the deposition of coke and metals on the catalyst which can poison the active sites of zeolites or block the pores [6]. Accumulation of ash on or inside the catalyst could also be responsible for catalyst deactivation, as it is reported that biomass originated alkali and alkaline earth metals (AAEMs) can poison the catalyst [1]. Like in conventional FCC (fluid catalytic cracking) processing, the catalysts deactivated by coke can be reused in a CFP process after being regenerated. In FCC regeneration, the catalyst is subjected to high temperature oxidative treatment to burn the coke off from the catalyst and thereby (partially) restore its activity [7]. In biomass CFP however, the coke-on-catalyst contains more oxygen and hydrogen than the coke-on-catalyst obtained in FCC processing. Regeneration of the catalysts thus yields water, apart from only CO_x ($CO + CO_2$), which for ZSM-5 and similar structured catalysts could lead to dealumination, and thus, loss of active (acid) sites [6,8].

All biomass materials contain ash-forming mineral nutrients in the form of cations which are bound onto the organic matrix of biomass at carboxylic and/or phenolic groups, or in the form of precipitates, such as a salt [9]. These indigenous and catalytically active minerals included in the biomass structure, such as alkali and alkaline earth metals (AAEM species, e.g. Ca, K, Mg, and Na), are known to catalyse cracking and several thermolysis reactions in the vapour phase and remould the chemical composition of a resulting pyrolysis liquid, and change the pyrolysis product distribution [10–15].

To prevent their diverse effects on pyrolysis product quality and distribution, the ash-forming elements can be removed from the biomass to some extent by washing with water, and more extensively by using an acidic washing liquid [16]. The main chemical composition of biomass is sensitive to the leaching conditions wherein harsh leaching can cause the degradation of hemicellulose [13,17]. Leaching also influences the chemical composition of pyrolysis liquid [18]. Even very small quantities of either alkali or alkaline earth metals in their chloride forms were shown to be sufficient to significantly alter the pyrolysis products. The presence of as little as 0.5 wt.% ash led to a strikingly different chemical speciation: in terms of levoglucosan yield, the order of strong to modest influence was found to be $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ [11].

While the conclusions concerning the effects of inorganic minerals on non-catalytic pyrolysis are well known, only few literature studies are available regarding the effects of ash and its constituents on the CFP of biomass. As of today, various projects have tried/are trying to push catalytic fast pyrolysis to the pilot scale or even to the commercial scale and have met varying levels

of success. Moreover, most of the studies in CFP literature concern the use of fresh catalyst; whereas, in large-scale practical applications, the spent (and coked) catalyst is regenerated (subjected to combustion) to be returned to the pyrolysis process [19]. Although, this is pretty much similar to the FCC process in an oil refinery, one aspect that is different – and thus, far not properly understood – is that biomass also contributes mineral matter (or ash) to the process. Through successive cycles of pyrolysis and catalyst regeneration, a considerable amount of this ash accumulates and could potentially affect the chemistry of pyrolysis as well as the stability and/or the activity of the catalyst. Mullen et al. [20] examined the accumulation of Ca, Cu, Fe, K, Mg, Na, and P from switchgrass on HZSM-5 during the catalytic pyrolysis in a fluidized bed reactor. The total amount of these elements was observed to be accumulated on HZSM-5 in a linear fashion during the successive use of the same catalyst sample. The catalytic activity, as measured by a drop in deoxygenation of the pyrolysis oil products and in selectivity of aromatic hydrocarbons, was decreased concurrent with the increase in inorganic elements on the HZSM-5. They concluded that some factors such as catalyst attrition could contribute to the decrease in catalytic activity, and the reactor designs decreasing the exposure of the raw biomass with the catalyst would be beneficial to catalyst lifetimes. Paasikallio et al. [21] performed the CFP of pine sawdust in VTT's Process Development Unit with a biomass throughput capacity of $20 \, kg \, h^{-1}$. A spray dried HZSM-5 catalyst was used. The changes in product yields, physical and chemical properties of the CFP products, and the changes in the properties and the structure of the catalyst were observed during a continuous run of over four days. Coke formation on the catalyst was observed to be heaviest at the beginning of the experiment, but then subsided over time. Catalyst micropore area and volume also decreased during the experiment; these were accompanied by apparent changes in the crystallinity and the structure of the catalyst. Biomass alkali metals (e.g. Ca, K, Mg, P, etc.) deposited on the catalyst in time, and a linear correlation was observed between this phenomenon and the decrease in the acidity of the catalyst.

To understand the role of indigenous or added inorganic compounds in CFP of biomass, and the potential ash/catalyst interactions that may take place in CFP, the influence of them on the distribution and composition of products resulting from the primary and secondary fast pyrolysis reactions has to be examined. Parameters such as the type and the condition of the catalyst, and the presence of inorganic constituents in the biomass, could be used to alter the relative rates of the biomass decomposition and subsequent vapour phase reactions, and eventually produce pyrolysis liquids with an improved composition. Fig. 1 shows the possible effects of the presence of the ash (whether or not accumulated during the process) on the activity of the catalyst in catalytic fast pyrolysis of biomass. Hypothetically, four different pathways can be distinguished on how the ash influences the vapour phase chemistry and the activity of the catalyst. It should be noticed that combined effects are possible too.

1. The catalytic effect of ash itself on the primary pyrolysis vapours results in the increased production of non-condensable gases (NCGs) and char.
2. Ash may crack some larger vapour phase molecules inaccessible to the catalyst's interior, to smaller ones which are capable of entering the catalyst pores.
3. Cracked vapours may then either be further reformed by the catalyst (a) or not (b).
4. Ash particles poison the catalyst and (negatively) affect the vapour conversion and the reaction chemistry.

The objective of this paper is to investigate the effects of indigenous and/or added biomass ash and its major constituents on the
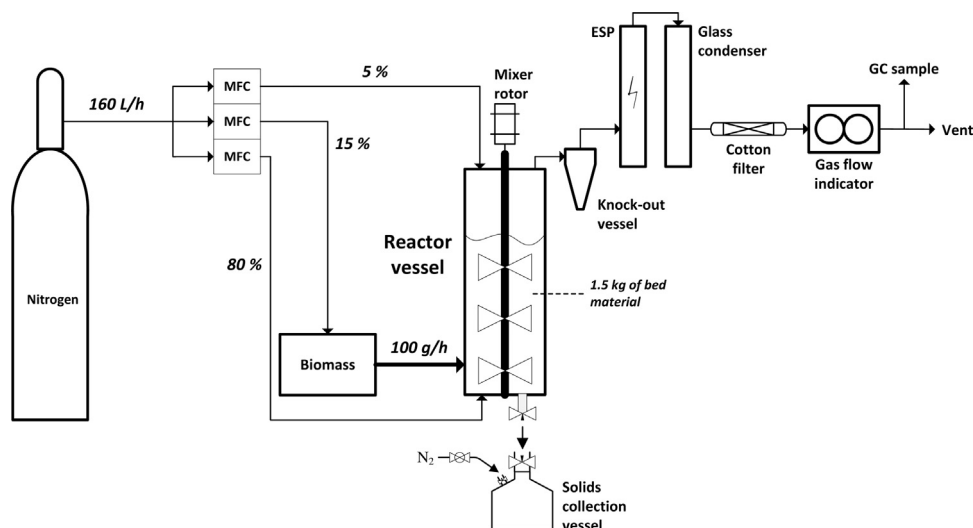
Fig. 1. Possible impact of ash on the catalyst and on the products in catalytic fast pyrolysis of biomass.

pyrolysis product yields and composition as observed in the non-catalytic and catalytic fast pyrolysis of pine wood. A discussion is provided on whether catalyst deactivation is caused merely by coke deposition and thermo-mechanical, chemical and structural changes of the catalyst, or by the presence of the biomass ash as well. The biomass ash could impact the catalyst properties directly (poisoning) or affect the pyrolysis vapours reaction pathways. For this purpose, non-catalytic and catalytic (in situ) fast pyrolysis experiments have been carried out with a ZSM-5 based catalyst in a laboratory scale, mechanically stirred bed reactor. The results of these experiments were compared with those of their pine-wood-ash added counterparts, and with the findings of an experiment in which the catalyst was successively reacted and regenerated eight times while the ash was accumulating in the bed material.

2. Experimental

2.1. Materials

In the experiments, pine wood (Bemap Houtmeel B.V., Bemmel, The Netherlands) was used as the reference biomass feedstock. Prior to the experiments, this feedstock was sieved to a particle size of 1–2 mm. The moisture and ash contents were 7.5 wt.% and 0.3 wt.% (on as-received basis, a.r.), respectively. The proximate analysis data, the elemental composition and the higher heating values (in as received and dry basis) of the pine wood are listed in Table 1.

Table 1
Properties of pine wood.

Proximate analysis (wt.%)	
Fixed carbon (d.b.)	14.96
Volatiles (d.b.) [ASTM E872-82]	84.76
Moisture (a.r.) [ASTM E871-82]	7.52
Ash (d.b.) [ASTM E1755-01]	0.33
Ultimate analysis (d.b.) [wt.%]	
C	47.1
H	5.9
O	46.4
N	0.04
S	0.06
Alkali metals (d.b.) [mg/kg]	
K	346.2
Na	10.1
Mg	112.8
Ca	767.0
HHV (a.r.) [MJ/kg][a]	16.91
HHV (d.b) [MJ/kg]	18.29

d.b.: dry basis.
a.r.: as received basis.
[a] Calculated by using the Milne formula [36].

Table 2
Chemical composition of ash obtained from pine wood, (d.b.) [wt.% in ash].

Element	wt.%	Element	wt.%
Ca	44.6	Ti	0.2
K	20.1	Pb	0.2
Mn	9.2	B	0.1
Mg	6.6	Cu	0.1
Si	5.6	Ni	0.03
S	3.3	Sn	0.02
Al	2.3	Cd	0.02
Fe	2.0	Cr	0.01
P	2.0	V	0.003
Co	1.4	Li	0.001
Zn	0.8	As	BDL
Ba	0.6	Mo	BDL
Na	0.6	Sb	BDL
Sr	0.2	Se	BDL

BDL: below detection limit.

Biomass ash was obtained by burning the pine wood at 600 °C in air. The chemical composition of ash obtained from pine wood is shown in Table 2. Calcium was found to be the major constituent in the ash (45 wt.%). Other major constituents were potassium (20 wt.%), manganese (9 wt.%) and magnesium (7 wt.%). The majority of the AAEMs present in the structure of biomass are reported to be in the form of water soluble salts such as chlorides, nitrates, carbonates and phosphates [22].

Silica sand (PTB-Compaktuna, Gent, Belgium) with a mean diameter of 250 μm and a particle density of 2650 kg/m^3 (compacted bulk density = 1660 kg/m^3) was used as the bed material in the non-catalytic experiments and blended with the catalyst and/or with the ash in the catalytic fast pyrolysis and ash addition experiments.

A spray dried heterogeneous ZSM-5 based catalyst was prepared and supplied by Albemarle Catalyst Company B.V. (Amsterdam, The Netherlands). The catalyst was received in the acid form and has been treated by the manufacturer accordingly. Prior to the delivery, this catalyst was calcined in air at 500 °C for 1 h to decrease the moisture content of the catalyst to below 1 wt.%. This was applied to prevent aging in the long term storage of the catalyst. Here, the term 'aging' represents the anticipated adsorption of water and/or CO$_2$ on the catalyst from its contact with air.

2.2. Experimental set-up and the analysis of pyrolysis products

Non-catalytic and catalytic pyrolysis experiments have been performed in a fully controlled, continuously operated lab-scale set-up as shown in Fig. 2.

Approximately 100 g of pine wood, at a feed rate of ca. 1.7 g·min^{-1}, is fed during every run, which could be determined by measuring the mass difference between pine in the storage

Fig. 2. Scheme of the pyrolysis set-up.

hopper and in the feeding screw, before and after each experiment. A pyrolysis temperature of 500 °C and a total inert gas (N_2) flow rate of ca. 160 L h^{-1} were used in all experiments. For the non-catalytic experiments 1.5 kg pure sand and for the catalytic experiments a catalyst–sand mixture of 1.5 kg (catalyst-to-sand mass ratio of 1:14) was used as the bed material. The reason for selecting a catalyst-to-sand weight ratio of 1:14 was to maintain the weight hourly space velocity WHSV [h^{-1}] at a value of around 1. The experimental run time (t_{run}) was kept at 60 min in order to produce sufficient pyrolysis liquid for different types of analyses (ca. 50 g/run) and to allow a sufficiently high accuracy for the mass balance. This long experimental run time also allowed the pine particles to be completely devolatilized at the specified reaction temperature.

The products obtained from non-catalytic and catalytic fast pyrolysis are divided into liquid products (organics and water), carbonaceous solids (the sum of char, heterogeneous coke, and system deposits) and non-condensable gases (NCGs). 'water', as a pyrolysis product, refers to the water content (in wt.%) of the total liquid product determined by Karl Fischer titration. Hence the amount of 'organics' can mathematically be expressed as: organics = liquid products – water. System deposits can be defined as the carbonaceous matter other than char in the case of the non-catalytic experiments, and an average value of ca. 5 wt.% was obtained after having been checked a number of times.

The pyrolysis liquids were stabilized with a known amount of tetrahydrofuran (THF) to form a homogeneous (single-phase) liquid mixture and analysed for the H$_2$O content (Karl Fischer titration, KF) and their chemical composition (GC × GC/MS–FID). For the detailed characterization of pyrolysis liquids, a combination of GC × GC–FID and GC × GC–TOF–MS was used to get a high chromatographic resolution and on the other hand maximal agreement between both chromatograms. All analytical tools and the procedures that are used to characterize the pyrolysis liquids are detailed in the papers of Yildiz et al. [3,19] and Djokic et al. [23]. The micro carbon residue (MCR) values of pyrolysis liquids were taken from an Alcor MCRT-160, which automatically executes a factory programmed ASTM D4530 test program.

The elemental composition of char samples were determined by a Thermo Scientific Flash 2000 Organic Elemental Analyser. The ultimate analysis of pine wood was performed using Interscience Carlo Erba element analyser for C,H,N and O. Inductively coupled plasma (ICP) equipment from spectro and atomic emission spectrometer (AES) from Vista were used for the other elements [24].

The composition of non-condensable gases was determined off-line using a micro GC (Varian 490-GC) equipped with two TCD detectors and two analytical columns. The following gaseous compounds were measured: CO, CO$_2$, CH$_4$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, C$_3$H$_8$ and H$_2$. The sum of C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$ and C$_3$H$_8$ will be further referred to as C$_{2+}$.

In this study, all the experiments and the analyses were performed at least in duplicate and averaged data are reported. The error bars in the figures represent standard deviations in absolute %'s. For the detailed information concerning the experimental unit, experimental procedures, yield calculations, and the collection and analyses of pyrolysis products, the reader is directed to our earlier publications [3,19].

2.3. Pyrolysis experiments

In this work, five types of pyrolysis experiments will be compared:

- A non-catalytic pyrolysis reference experiment (denoted as "NC").
- Non-catalytic pyrolysis after addition of biomass ash (denoted as "NC + ash").
- Catalytic pyrolysis with fresh catalyst as a reference experiment (denoted as "R0").
- Catalytic pyrolysis with fresh catalyst and added biomass ash (denoted as "R0 + ash"), and finally
- Catalytic pyrolysis with catalysts obtained after eight successive reaction/regeneration cycles (denoted as "R8").

The values obtained from five non-catalytic and three catalytic experiments with fresh catalyst were averaged to define the reference cases "NC" and "R0", respectively. The mass balance closures for all experiments varied from 92 to 99 wt.%, while the scatter in measured data was always less than 5%. The standard deviations are shown in Fig. 3. Operating conditions for these experiments can be found elsewhere [19]. For all experiments, an identical experimental procedure was applied.

Bed materials obtained from the reference R0 experiments (char, sand and the spent catalyst mixture) were removed from the reactor after pyrolysis. Small amounts of char and spent catalyst/sand mixture were taken for their compositional analyses, and the rest was subjected to a two-step regeneration procedure (oxidative treatment to burn the coke and remove the carbon as

CO_2) in a muffle furnace (based on the procedure proposed by Aho et al. [25]). Here, the oven temperature was increased from ambient to 250 °C (4.5 °C min^{-1}), and kept isothermal at 250 °C for 40 min. Then the temperature was raised to 600 °C (5 °C min^{-1}), and kept at 600 °C for 5 h. Finally the catalyst–sand mixture, regenerated in this way, was stored in the oven at 105 °C until the next experiment. The regenerated bed materials obtained from the reference R0 experiments were introduced back to the reactor and subsequent experiments were carried out (R1). This reaction/regeneration sequence was continued up to an 8th regeneration cycle which was denoted as "R8". The experiments were started with three parallel batches, which were combined to two parallel batches after the sixth sequence to make up for the amount of material used for analyses and/or losses.

The ash that was initially present in the pine wood, and later in the char, was not removed actively during the successive regeneration steps but most likely remained in the bed material and thus may accumulate along the reaction/regeneration cycles. For a comparison, the same quantity of biomass originated ash that would have been accumulated in the bed material after eight regeneration cycles (ca. 3 g) was added to pure sand (NC + ash) as well as to fresh catalyst–sand blend (R0 + ash). It is important to note that the predominant ash volatilisation mechanisms do not occur to a significant extent, neither at 600 °C (ashing temperature) nor at 500 °C (pyrolysis reaction temperature) [26]. Three identical experiments were performed for each case and the results were averaged.

3. Results and discussions

3.1. Effect of ash on the product yields

Fig. 3 shows the average product yield distribution on feedstock weight (as received) basis obtained from ash addition experiments compared to the reference experiments (NC, R0 and R8). The scatter in the product yields is less than 5% indicating sufficient reproducibility to draw conclusions with respect to the trends in the experiments.

The highest organics yield, and the lowest water, carbonaceous solids (CS) and NCG yields were obtained in the NC experiments. The addition of ash (NC + ash) had only a marginal effect in non-catalytic pyrolysis; the yield of organics decreased by 0.5 wt.%, and CS and NCG yields increased by almost 1 wt.%. Actually these values are within the experimental error, but their trends are in line with the literature [16,27]. Comparison of the catalytic experiment
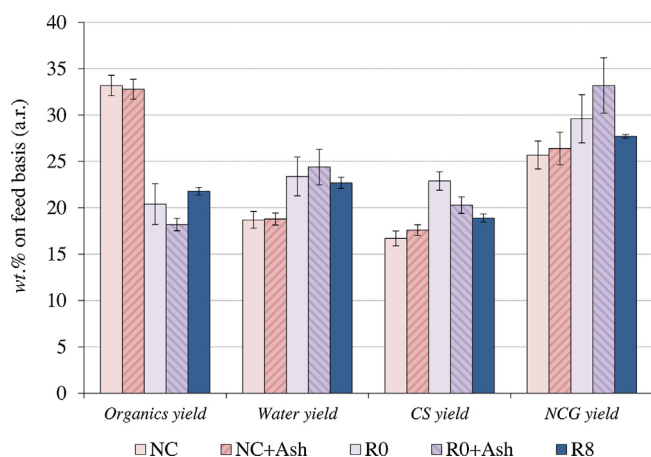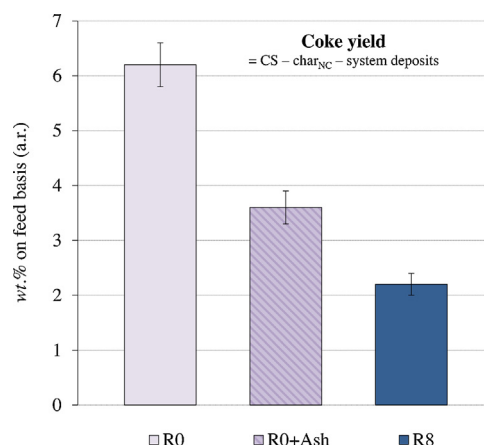

Fig. 4. Calculated coke yield obtained from ash-added catalytic experiments (R0 + ash) compared to those of catalytic fast pyrolysis with fresh catalyst (R0), and the 8th cycle of catalyst regeneration experiments (R8). Fast pyrolysis of pine wood at 500 °C.

with fresh catalyst (R0) with the one having ash added (R0 + ash), shows a larger difference in results. The presence of the added ash in catalytic fast pyrolysis induced an extra decrease in the yield of organics and carbonaceous solids by 2 wt.% for both. On the contrary, the water yield increased by 1 wt.% and the non-condensable gas yield increased by 4 wt.%, presumably due to the presence of ash (vapour cracking). The decrease in the yield of carbonaceous solids after ash addition (specifically the calculated coke, see Fig. 4 – R0 vs. R0 + ash) points to a suppression of coke formation on the catalyst. Similarly, increases in both water and NCG yields and decreased yields of organics are indicative for additional cracking activity induced by the catalyst, the ash or a combination thereof. Because the ash content in R0 + ash is much higher than in R0 (3 wt.% versus ca. 0.3 wt.%, respectively, on feedstock basis), vapour cracking by ash components (Path 2 of Fig. 1), or in series by both the ash and the catalyst (Path 3a of Fig. 1) is likely to occur.

Comparing the yields obtained in R0 + ash and R8, the differences are more pronounced. The organics yield of R8 is 4 wt.% higher, while the water, CS and NCG yields are 2, 1, and 6 wt.% lower, respectively. The presence of ash cannot be the only reason to account for these differences in product distribution, as the amount of ash present in pyrolysis is equal for both cases. However, the observed differences in pyrolysis products yields can be due to loss of activity of the catalyst itself, or another way of incorporation of the ash components in or on the catalyst. Although, the loss of a part of the catalyst after eight reaction/regeneration cycles could be another cause, this has not been observed.

The individual yields of char and the system deposits were assumed to be ca. 12 wt.% and ca. 5 wt.%, respectively for all the experiments, due to the fact that each experiment has been carried out under identical process conditions; this has been verified a number of times. Besides, the residence time of the pine wood particles in the bed (t_{run} = 60 min) was always sufficiently long to allow for a complete devolatilization at the adjusted reaction temperature (500 °C). Hence, the differences in the yields of carbonaceous solids must indicate a change in the coke yield.

Fig. 4 shows the changes in calculated coke yield for three individual groups of catalytic experiments, viz. R0, R0 + ash and R8. After ash addition (R0 + ash), the coke yield decreased by 3 wt.% compared to R0. An explanation could be that the minerals are interfering with the active sites inside the catalyst particles, effectively reducing the catalyst activity (Path 4 in Fig. 1). Another possible explanation could be that the metals contained in the ash favour the vapour cracking (Path 2 in Fig. 1) and/or inhibit the formation of coke precursors.

Fig. 3. Product yields obtained from ash addition experiments compared to those of the reference, non-catalytic (NC), the catalytic with fresh catalyst (R0), and the 8th cycle of catalyst regeneration (R8) experiments. Fast pyrolysis of pine wood at 500 °C.

Table 3

Average non-condensable gas compound yields obtained from ash addition experiments. Values are compared to the reference, the non-catalytic (NC), the catalytic fast pyrolysis with fresh catalyst (R0) experiments, and the 8th cycle of catalyst regeneration experiments (R8). Product yields and standard deviations are represented in wt.% on feed basis (a.r.) and absolute %'s, respectively. Fast pyrolysis of pine wood at 500 °C.

	NC	NC + ash	R0	R0 + ash	R8
CO	13.0 ± 0.8	13.4 ± 1.1	16.2 ± 1.7	17.3 ± 1.4	14.9 ± 0.3
CO_2	10.0 ± 0.7	9.9 ± 0.5	10.1 ± 1.1	12.1 ± 1.2	9.7 ± 0.5
CH_4	1.6 ± 0.1	2.1 ± 0.2	1.3 ± 0.2	1.7 ± 0.0	1.6 ± 0.1
C_{2+}	0.38 ± 0.02	0.41 ± 0.04	0.87 ± 0.11	0.86 ± 0.18	0.54 ± 0.06
H_2	0.10 ± 0.01	0.12 ± 0.01	0.05 ± 0.00	0.08 ± 0.00	0.07 ± 0.00
CO_x [a]	22.9 ± 1.5	23.2 ± 0.5	26.3 ± 2.7	29.4 ± 2.6	24.6 ± 0.2
CO/CO_2 [b]	1.30 ± 0.03	1.35 ± 0.04	1.61 ± 0.09	1.43 ± 0.03	1.54 ± 0.10

[a] CO_x yield is the sum of CO and CO_2 (in wt.%).
[b] CO/CO_2 ratio is dimensionless (wt./wt.).

The coke yield of R8 was 4 wt.% and 1 wt.% lower than of R0 and R0 + ash respectively. When the results of R0 + ash and R8 are compared, it is observed that although principally the same amount of ash is present in both cases, the coke yields are different. It should be noticed here that, during the eight reaction cycles changes occur on the catalyst/sand mixture. Obviously the apparent reduction in catalytic activity cannot be explained only by the presence of ash. Multiple reaction and catalyst regeneration cycles cause thermo-mechanical, chemical and/or physical changes in the catalyst structure, likely as a consequence of poisoning, fouling and attrition. The latter might even cause the catalyst content of the sand/catalyst mixture to be lowered. Hence, the lower coke yield found in R8 is largely due to an apparent reduction in catalyst activity as a consequence of the repeated regeneration of the catalyst/sand mixture.

3.2. Effect of ash on the yields of the individual non-condensable gas compounds

To further clarify the effect of ash on the cracking reactions, the yields of the individual non-condensable gas compounds are summarised in Table 3. Like in Fig. 3, the presence of ash seems to have a small effect in the case of the non-catalytic experiments. For both the non-catalytic (NC) and catalytic with fresh catalyst (R0) experiments, the presence of ash promoted the CH_4 and H_2 yields, while C_{2+} yields remained unaffected. The increase in CH_4 and H_2 yields may be attributed to vapour gasification reactions being enhanced by the minerals in ash. The reduced H_2 yield observed in R0, if compared to NC, suggests that hydrogen is consumed in the catalysed reactions (e.g. dehydration, hydrogenation of olefins or aromatics). Comparing the catalytic pyrolysis experiments R0 and R0 + ash seems to favour decarbonylation (CO production) and decarboxylation (CO_2 production) reactions, with a corresponding yield increase of 1 wt.% and 2 wt.%, respectively. As previously mentioned, the effect of ash on NCG production could be four-fold (Fig. 1). The decrease in the CO/CO_2 ratio from 1.6 down to 1.4 shows that decarboxylation reactions are favoured in the presence of ash. The increase in CO_x (sum of CO and CO_2) yields is due to secondary vapour cracking reactions which is in line with the findings reported in the literature [16]. The yields of all non-condensable gas compounds in R8 were lower than the ones obtained from the R0 + ash experiments, despite of a theoretically similar amount of ash present in both cases. On the other hand, the values obtained for NC + ash were quite close to the ones in R8 which indicates that (i) the catalyst has lost most of its apparent activity after 8 reaction/regeneration cycles and/or is partially lost, thereby yielding pyrolysis product distributions more akin to the non-catalytic case and (ii) some differences with respect to NC can be attributed to ash accumulation or some combined catalyst-ash effect. Both the yields of CO and CO_2 decreased by 2 wt.% in R8, if compared to R0 + ash. The higher CO/CO_2 ratio for R0 showed that the type of deoxygena-

tion via gaseous species is different than the experiments wherein the ash is involved (R0 + ash and R8). This suggests that the change in the activity of the catalyst is not only related to the presence of ash but also to physical and chemical changes in the structure or in the composition of the catalyst/sand mixture.

3.3. Effect of ash on the composition of pyrolysis liquids

Fig. 5 shows the yields of compounds detected by GC × GC/MS–FID analysis. They are being classified according to their functional group, and ordered by the type of experiments. Included are sugars, aldehydes, acids, furans, ketones, phenols, aromatics and others (unclassified oxygenates such as 1-hydroxy-2-propanone). Table 4 shows details of the most prevalent individual compounds detected via GC × GC/TOF–MS analysis and quantified by GC × GC/MS–FID. For the quantification procedure, the reader is referred to the paper of Djokic et al. [23]. It should be taken into account that the yields shown in Fig. 5 and Table 4 were normalized and expressed on an as-received (a.r.) feed basis.

Table 4

Yields of the most prevalent compounds in pyrolysis liquid (GC × GC/MS–FID detectable only) in case of ash addition experiments, compared to the reference, non-catalytic (NC), catalytic fast pyrolysis with fresh catalyst (R0) experiments, and the 8th cycle of catalyst regeneration experiments (R8) of pine wood at 500 °C (wt.% averages on feed basis (a.r.)).

|	NC	NC + ash	R0	R0 + ash	R8
Sugars (3 compounds)	3.79	3.07	0.04	0.31	2.09
Levoglucosan	3.22	2.58	0.00	0.29	1.84
Aldehydes (2 compounds)	0.67	0.63	0.00	0.00	0.00
Hydroxyacetaldehyde	0.67	0.60	0.00	0.00	0.00
Acids (9 compounds)	2.09	2.46	0.97	1.28	1.64
Acetic acid	1.50	1.99	0.57	0.94	1.16
Propanoic acid	0.29	0.16	0.07	0.09	0.13
Furans (12 compounds)	0.57	0.58	0.28	0.26	0.12
Furfural	0.22	0.15	0.06	0.08	0.02
Ketones (9 compounds)	0.83	0.66	0.40	0.39	0.66
2-Cyclopenten-1-one	0.16	0.16	0.14	0.17	0.34
Phenols (24 compounds)	2.49	2.31	2.31	2.01	3.16
1,2-Benzenediol	0.51	0.46	0.37	0.32	0.50
4-Methyl-1,2-benzenediol	0.61	0.59	0.43	0.36	0.69
4-Ethylcatechol	0.29	0.26	0.21	0.17	0.34
2,4-Dimethyl-phenol	0.19	0.14	0.21	0.16	0.21
4-Methyl-phenol	0.11	0.11	0.28	0.24	0.27
2-Methyl-phenol	0.10	0.10	0.17	0.16	0.18
Phenol	0.08	0.08	0.28	0.24	0.24
Aromatics (19 compounds)	0.00	0.00	0.47	0.45	0.44
Xylene (m,p)	0.00	0.00	0.03	0.01	0.01
1-Methyl naphthalene	0.00	0.00	0.24	0.18	0.09
Methyl-1H-indenes	0.00	0.00	0.06	0.07	0.06
Indene	0.00	0.00	0.03	0.03	0.02
Indane	0.00	0.00	0.01	0.01	0.01
Others (21 compounds)	1.69	2.46	0.67	1.03	1.46
1-Hydroxy-2-propanone	1.08	1.45	0.20	0.47	0.80
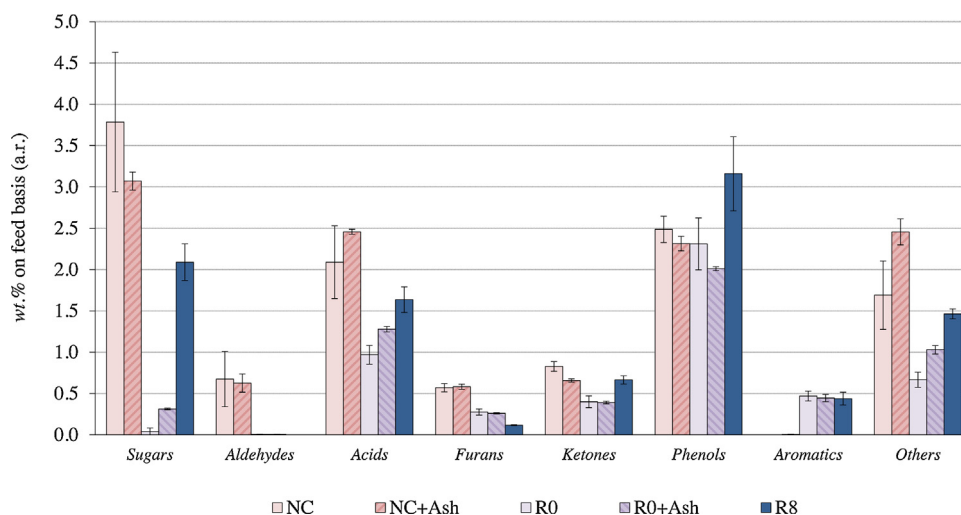
Fig. 5. Yields of functional groups in pyrolysis liquid (GC × GC/MS–FID detectable only) are shown for ash addition experiments, compared to the reference, non-catalytic (NC), the catalytic fast pyrolysis with fresh catalyst (R0), and the 8th cycle of catalyst regeneration experiments (R8). Fast pyrolysis of pine wood at 500 °C.

As shown by Fig. 5 and Table 4, the chemical composition of the detectable part of the pyrolysis liquid is significantly influenced by the presence of the catalyst. Besides, effects can be observed caused by the presence of the ash. Comparing NC and R0, the most important observations related to the presence of the catalyst were the complete suppression of the sugars and aldehydes as well as a significant decrease in acids, furans, ketones, and compounds classified as "others" (i.e. unclassified oxygenates). The quantity of the aromatics was increased as well.

In fast pyrolysis, the mineral salts/ash present in biomass lowers the activation energy of reactions leading to the direct formation of the lower molecular weight decomposition species of cellulose, such as; glycolaldehyde (hydroxyacetaldehyde), formic acid, acetol and gas compounds. The reason of decreased levoglucosan yields is that the preferential activation of these reactions reduces the amount of cellulose available for the reactions that produce levoglucosan [11,28,29]. In our study, the presence of ash (NC vs. NC + ash) revealed clear changes in the yields of some chemical species such as a decrease in the levoglucosan yield and increased yields of acetic acid and 1-hydroxy-2-propanone (acetol) (Table 4), which are in line with the literature. The presence of potassium and calcium in the form of $CaCl_2$ has a decreasing effect on the levoglucosan yield [11] while magnesium has the opposite effect [13]. Moreover, alkaline earth metal chlorides ($MgCl_2$, $CaCl_2$) were reported to increase the char yield in cellulose pyrolysis at 400 °C while decreasing the yield of levoglucosan [30]. This would impact the observed coke yield, since it is assumed here that char yield is always the same as for non-catalytic (see also Section 3.1). In order to achieve higher levoglucosan yields, biomass would need to be demineralized down to certain concentrations [11]. By the removal of alkali and alkaline earth metals, increased yields of lignin-derived oligomers in the pyrolysis liquid were observed as well [18]. The decrease in phenols both in non-catalytic and catalytic experiments with and without ash (Table 4) was in line with this observation.

In CFP of biomass with acidic zeolites, the catalyst is known to promote cracking reactions leading to production of highly deoxygenated and hydrocarbon-rich compounds via acid catalysed dehydration, decarbonylation and decarboxylation reactions [12,31]. In the case of experiments with fresh catalyst with and without ash addition (R0 and R0 + ash), increases in yields of sugars, acids and other oxygenates were observed after the addition of ash. Especially the increase in sugar yields, which was not the expected scenario in the presence of the ash (as explained before),

revealed that the catalytic activity was changed by the addition of the ash. This can be explained by the deposition or adsorption of ash derived chemical species (e.g. AAEMs) on the catalyst surface, thereby blocking either the active sites or the pores inside the catalyst and reducing its activity. On the other hand, the production of aromatics and ketones was not affected by the presence of ash. After several regeneration cycles the situation is again different. For R8, compared to R0 + ash the yields of sugars increase (from 0.3 wt.% to 1.8 wt.%), together with acids (acetic acid from 0.9 wt.% to 1.2 wt.%), ketones (doubled 2-cyclopenten-1-one yield from 0.2 wt.% to 0.3 wt.%), phenols (increases in catechol, 4-methyl-catechol and 4-ethyl-catechol) and other oxygenates (increase in for example 1-hydroxy-2-propanone from 0.5 wt.% to 0.8 wt.%). Conversion of aldehydes in both cases, and a similar yield in aromatics revealed that the catalyst still had a certain activity, even after eight cycles. Unfortunately, the significant difference regarding the production of detectable phenols cannot be explained very well in this stage of research. R8 shows a level higher than all other cases. In our earlier paper concerning the effect of successive catalysts regeneration [19], the rising level of phenols was observed particularly during the last three cycles.

While looking at the results shown in Fig. 5, it should be kept in mind that the compound conversions may not be limited only by the reduction of acid sites in the catalyst's interior, but also by the presence of sufficient reaction precursors in the vapour phase, the catalyst accessibility, and/or changes in the ratio of sand to catalyst due to catalyst attrition or selective removal (relatively large difference in density and particle size). Overall, it can be concluded that the deactivation of the catalyst is not only related to the presence of ash but also caused largely by the thermo-mechanical, chemical or physical changes (e.g. poisoning, fouling, attrition, and amount) occurring during the eight reaction/regeneration cycles.

3.4. Effect of biomass ash on the elemental distribution over various pyrolysis products

Table 5 shows the elemental distribution over various pyrolysis products (organics, water, char, coke, and NCGs) obtained from the ash addition experiments, compared to the reference experiments (NC, R0 and R8). The presence of ash in case in non-catalytic pyrolysis had almost no effect regarding the elemental distribution over the various pyrolysis products. On the other hand, the addition of ash in R0 + ash caused some slight changes in the elemental distribution when compared to the catalytic experiments

Table 5
Elemental distribution over various pyrolysis products obtained in ash addition experiments. Values are compared to the reference, the non-catalytic (NC), the catalytic fast pyrolysis with fresh catalyst (R0) experiments, and the 8th cycle of catalyst regeneration experiments (R8). Values shown are mass fractions in %, relative to the carbon, hydrogen, oxygen present in the biomass feed. Fast pyrolysis of pine wood at 500 °C.

	NC	NC + ash	R0	R0 + ash	R8
Carbon					
Organics[a]	59.4	60.2	51.5	49.9	55.3
Water[b]	–	–	–	–	–
Char	19.9	19.4	19.7	19.7	19.6
Coke[c]	5.1	5.1	11.2	11.2	7.5
NCG[d]	15.6	15.3	17.6	19.2	17.6
Hydrogen					
Organics[a]	45.8	45.0	33.2	28.9	36.4
Water[b]	35.2	35.4	43.1	45.9	42.7
Char	6.7	6.5	6.4	6.4	6.3
Coke[c]	4.5	4.5	9.9	9.9	6.7
NCG[d]	7.8	8.6	7.4	8.9	8.0
Oxygen					
Organics[a]	34.2	33.4	17.8	11.2	23.5
Water[b]	35.8	35.5	43.2	46.1	42.9
Char[e]	1.9	3.1	2.9	4.0	1.2
Coke[c]	4.3	4.3	9.4	9.4	6.3
NCG[d]	23.8	22.6	25.6	28.4	25.1

[a] Calculated by difference.
[b] Based on the results of Karl Fischer analyses.
[c] Coke refers to coke on catalyst. The elemental composition of coke was obtained (the given values were averaged) from Williams and Horne [37].
[d] Derived from micro-GC analyses.
[e] Oxygen in char was calculated by difference.

Table 6
MCR values and H/C ratios of the liquid products (organics + water) obtained from ash addition experiments, compared to the reference, non-catalytic (NC), the fresh catalyst (R0), and the 8th cycle of catalyst regeneration experiments. Fast pyrolysis of pine wood at 500 °C.

	NC	NC + ash	R0	R0 + ash	R8
MCR (wt.%)	8.25	7.14	2.50	3.67	3.42
H/C	1.36	1.33	1.48	1.50	1.43

non-catalytic fast pyrolysis of pine, the addition of ash reduced the MCR value from 8.3 wt.% to 7.1 wt.%. In the literature, the MCR of non-catalytic pyrolysis liquid is reported to be in the range from 16 to 20 wt.% [35]. The lower MCR values found in this study may be the result of significant cracking of the vapours as a consequence of relatively long hot vapour residence times. In case of catalytic fast pyrolysis with fresh catalyst, an opposite effect of ash addition was observed; the MCR value increased from 2.5 wt.% to 3.7 wt.%. This could be caused by deactivation of the catalyst due to adsorption/clogging with biomass-derived minerals – which would increase the MCR. And consequently, the decreasing effect of ash on the MCR (through more intense cracking) is more than negated by the reduction of catalyst activity due to the mineral contamination of the catalyst (which increases the MCR). The MCR value of R8 was 3.4 wt.% and slightly smaller than that of R0 + ash. Compared to that of non-catalytic experiments, the H/C ratio of the liquid product increased in case of the catalytic pyrolysis. However, the addition of ash (both in non-catalytic and catalytic cases) seemed to have almost no effect on the H/C ratio of the liquid product.

4. Conclusions

Accumulated ash may affect the efficiency of the catalyst by its influence on the composition of the primary pyrolysis vapours to be reformed by the catalyst. Ash concentrations as low as ca. 3 wt.% relative to the amount of pine wood fed, and ca. 0.002 wt.% relative to the amount of bed material, were found sufficient to have a direct effect on the yield and composition of the catalytic fast pyrolysis products. Although, the effects are different in their details, the impact of accumulated ash in catalytic fast pyrolysis is comparable with that of selective catalyst losses and/or catalyst deactivation. The latter could then be well enhanced by the accumulated ash. To overcome the drawbacks of biomass ash in catalytic fast pyrolysis, the char (which contains a vast majority of the biomass ash) has to be physically removed from the catalyst before the regeneration step. The biomass feedstock used in this study (pine wood) is a low-ash feedstock. With the use of high-ash containing feedstock, and the larger number of reaction/regeneration cycles desired in future large scale installations, the effect of ash will be even more dramatic. Future research should reveal whether the observed trends will persist after many more reaction/regeneration cycles, and how long it takes for the catalyst to completely deactivate. Strategies to reduce the minerals burden in the catalytic fast pyrolysis process could extend the lifetime of the catalyst.

with fresh catalyst only (R0). The carbon content of the organic fraction of pyrolysis liquid slightly decreased by 2% while it increased by the same amount in NCGs. That supports the hypothesis that ash minerals are able to crack the larger molecules of the primary vapours (Path 2 in Fig. 1). Char and coke yields were not affected. For hydrogen and oxygen, the changes are clearer, as they decreased by 4% and 7%, respectively. The hydrogen and oxygen yields for the aqueous phase (associated with the increase in the water yield) increased by 3% for both. Hydrogen and oxygen yields in the non-condensable gases increased by 2% and 3%, respectively. These findings revealed that, in line with the above shown results, the presence of ash increased the water and NCG production (particularly CO_2).

When the results obtained in the R8 experiment were compared to R0 + ash significantly more carbon, hydrogen and oxygen from the feed ended up in the organics; they were increased by 5%, 8% and 12%, respectively. These results show that the redistribution of C, H and O from the feedstock towards the pyrolysis product fractions in the R8 experiments was more similar to those of non-catalytic (NC) experiments which can be interpreted as a sign of selective catalyst deactivation and/or loss. The decreased elemental contents in coke and NCGs are in line with that suggestion; see also Fig. 4 and Table 3.

When the aim is to produce pyrolysis liquids that are compatible with petroleum feedstock, the final product is usually evaluated by its O/C and H/C ratio. A low O/C and a high H/C ratio indicate a better quality liquid [32]. The distillability of the pyrolysis liquid is related to its H/C ratio and could be determined by the micro carbon residue (MCR) value. In general, oxygen rich aromatic feedstock are characterized by high carbon residues, low H/C ratios and are highly polar, and they are forming considerable amounts of coke (2–8 wt.%) during cracking [33]. Moreover, the coking tendency of the pyrolysis liquid increases with increasing MCR values which is an indication of heavy oxygenated components. In biomass fast pyrolysis, the presence of a catalyst reduces the micro-carbon residue (MCR) of the pyrolysis liquid [34,35]. Table 6 shows the MCR values and H/C ratios of the liquid products (organics + water). In

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